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(54) AQUEOUS SOLUTION OR AQUEOUS DISPERSION OF COPOLYMER HAVING WATER-REPELLING PROPERTY, ITS PRODUCTION AND AQUEOUS COATING COMPOSITION CONTAINING THE SAME

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain the subject aqueous solution

useful as a coating resin capable of forming a coating film having

excellent water-repellence and water resistance by copolymerizing a

mixture containing a monomer having a specific structure, a

monomer having an alkoxysilyl group, an ethylenic unsaturated

MONITOR, INC.

SOLETON. THE OBJECTIVE aqueous solution is produced by

copolymerizing a monomer mixture containing (wt %): 3-*t*-butyl-6-*tert*-butyl-4-vinylphenol

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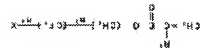
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unsaturated monomers.



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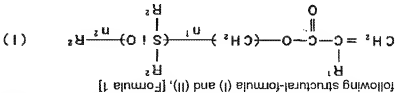
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CLAIMS

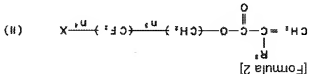
[Claim(s)]

[Claim 1](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by



integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)



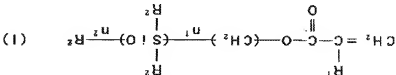
[Formula 2]

(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

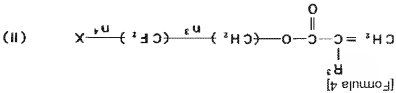
The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta- ethylenic unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others

are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight.

[Claim 2](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by



(Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows the integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6, respectively.)



(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

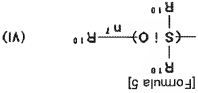
The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has unsaturated monomer 1 to 25 % of the weight, and the monomeric mixture which contains 0 to 95 % of the weight for alpha in which others are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer, A manufacturing method of the copolymer solution which has the water repellence which adds water and a neutralizer in the copolymer (A) solution produced by performing a radical polymerization in an organic solvent, and is characterized by aqueous-ization or forming mixture powder, or a water dispersion.

[Claim 3] A manufacturing method of the copolymer solution according to claim 2 in which an organic solvent contains alcohol of the carbon numbers 1-8 10 % of the weight or more, or a water dispersion.

[Claim 4] After mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decantalization is possible, water and a neutralizer are added, and it is a manufacturing method of aqueous-izing, the copolymer solution according to claim 2 or 3 formed into mixture powder, or a water dispersion.

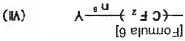
[Claim 5] a copolymer (A) solution — after [or] adding a surface-active agent which has a water-repellent group in a copolymer (A) and a mixed solution of (B) — a manufacturing method of copolymer solution of claims 2 thru/ or 4 aqueous-izing or given in any 1 paragraph which carries out mixture powder, or a water dispersion.

[Claim 6] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural formula (VI), or a water dispersion.



(R^{10} shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n^7 shows the integer of 5-200, respectively.)

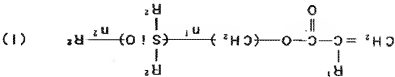
[Claim 7] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural formula (VII), or a water dispersion.



(γ shows a hydrogen atom or a fluorine atom among a formula, and n^8 shows the integer of 1-30, respectively.)

[Claim 8] A manufacturing method of copolymer solution which obtains copolymer solution according to claim 1 or a water dispersion using an emulsion polymerization method, or a water dispersion.

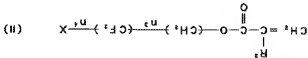
[Claim 9] (a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by following structural formula (I) and (II), [Formula 7]



(Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows the

integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)



(the inside of a formula, and R^2 -- a hydrogen atom or a methyl group -- X shows a hydrogen atom or a fluorine atom, n^1 shows the integer of 1-8, and n^2 shows the integer of 1-30, respectively.)

A monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carbonyl group, alpha which has one sort of functional groups chosen from a group of a sulfonic group and an amino group, and beta- ethylenic

unsaturated monomer 1 to 25 % of the weight, And a diisocyanate constituent which contains copolymer solution or a water dispersion which has the water repellence which carries out copolymerization of the monomeric mixture which contains alpha in which others are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight as a vehicle component.

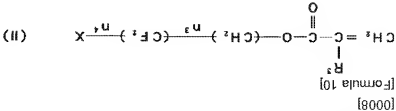
[Claim 10]The diisocyanate constituent according to claim 9 in which a monomeric mixture contains a monomer

which has the (e) carbonyl group one to 30% of the weight.

[Claim 11]The diisocyanate constituent according to claim 10 which contains a hydrazine derivative which has at least two -NH-NH₂ content groups in one molecule as a cross linking agent.

[Translation done.]

[0007] Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows the integer of 1-10 and n^2 shows the integer of 5-20 for a phenyl group or the alkyl group of the carbon numbers 1-6, respectively.

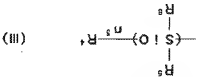


[0009] (the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta-ethylenic unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others are [being (d) and] copolymerizable, and beta-ethylenic unsaturated monomer zero to 95% of the weight, And the distemper constituent which contains the manufacturing method and this copolymer solution, or a water dispersion as a vehicle component is provided.

[0010] [Embodiment of the invention] A least one sort of monomers (a) chosen from the monomer shown by above structural-formula (i) and (ii) in this invention, Water repellence is given to a copolymer and any 1 way of the monomer (a-2) containing the fluoride shown by the monomer (a-1) and the above-mentioned structural-formula monomer (ii) which have a polysiloxane chain shown by the above-mentioned structural-formula (i), or both can be used. [0011] In the monomer (a-1) shown by the above-mentioned structural-formula (i), although R^1 is a hydrogen atom or a methyl group and R^2 is a phenyl group or an alkyl group of the carbon numbers 1-6, there is not necessarily the necessity that its mutually the same, n^1 — the integer of 1-10, and n^2 — 5-200 — it is an integer of 15-150 preferably. Since the hydrophilic nature of a copolymer runs short and it becomes poor [water solubility or water dispersibility] when water repellence with n^2 sufficient by less than five is not acquired but it exceeds 200 conversely, it is not desirable. As an example of this monomer (a-1), "Silaplane FM-071", "Silaplane FM-072", "Silaplane FM-075" (all are the Chisso Corp. make), etc. are mentioned with a commercial item. [0012] In the monomer (a-2) shown by the above-mentioned structural-formula (ii), R^3 is a hydrogen atom or a methyl group, and X is a hydrogen atom or a fluorine atom, n^3 is an integer of 1-8 and n^4 is an integer of 1-30. If n^4 exceeds 30, since mixing nature with other monomers and copolymer are inferior, and hydrophilic nature runs short and it will become poor [water solubility or water dispersibility], it is not desirable, as the example of this monomer (a-2) — 2, 2', and 2-tetrafluoroethyl (meta-) acrylate, 2,2,3,3-tetrafluoro propyl (meta) acrylate, 2-(pentafluorooctyloxy) ethyl (meta) acrylate, in commercial items, such as 2-(nonadecafluorodecyl) ethyl (meta) acrylate, "FAMAC" (made by Nippon Mektron, Ltd.), "screw coat 8FM", "screw coat 17FM" (all are the OSAKA ORGANIC CHEMICAL INDUSTRY, LTD. make), etc. are mentioned. [0013] The monomer (b) which has alkoxy silyl groups in this invention has the alkoxy silyl groups shown by following structural-formula (iii), [0014]

[Formula 11]

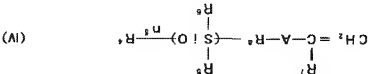


[0015] (Among a formula, as for R^5 and R^6 , R^4 is the same or different in the alkyl group of the carbon numbers 1-10, and n^5 shows the integer of 1-4 for a phenyl group, the alkyl group of the carbon numbers 1-6, or the alkoxy group of the carbon numbers 1-10, respectively.) When n^5 is two or more, R^5 comrade and a comrade's R^6 may be the same, or may differ from each other.

The monomer shown by following structural-formula (IV) and (V) as the example of representation can be mentioned.

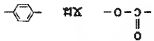
[0016]

[Formula 12]



[0017] (inside of a formula, and A) [0018]

[Formula 13]



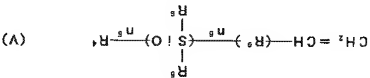
[0019] R^7 shows a hydrogen atom or a methyl group, and R^8 shows the divalent aliphatic-saturated-

hydrocarbon group of the carbon numbers 1-6, respectively, R^4 , R^5 , R^6 , and n^5 have the respectively same

meaning as the above.

[0020]

[Formula 14]



[0021] (R^6 shows the divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6 among a formula,

and n^5 shows 0 or 1, R^4 , R^5 , R^6 , and n^5 have the respectively same meaning as the above.

In the above-mentioned structural-formula (I) and (V), as a divalent aliphatic-saturated-hydrocarbon group of the

carbon numbers 1-6 shown by R^8 and R^9 , The alkylene group of a straight chain or the letter of branching, for

example, methylene, ethylene, propylene, 1,2-, 1,3- or 2,3-butylene, tetramethylen, ethylethylen,

pentamethylen, a hexamethylen group, etc. can be mentioned. As an alkyl group of the carbon numbers 1-6

shown by R^5 and R^6 , The alkyl group of a straight chain or the letter of branching, for example, methyl, ethyl, n-

propyl, isopropyl, n-, i-, sec- or tert-butyl, n-pentyl, isopentyl, neopentyl one, n-hexyl, isohexyl, 1-methylpentyl, etc.

are mentioned. n-heptyl, 2-ethylhexyl, n-octyl, n-nonyl, n-decyl, etc. other than what was illustrated as an alkyl

group of the carbon numbers 1-6 shown by R⁵ and R⁶ as an alkyl group of the carbon numbers 1-10 shown by R⁴ are mentioned further. As an alkoxy group of the carbon numbers 1-10 shown by R⁵ and R⁶, Alkoxy group of straight chain or letter of branching, for example, methoxy, and ethoxy **, n-propoxy, isopropoxy, n-, i-, sec- or tert-butoxy, n-pentoxo, isopentoxo, n-hexyloxy, isohexyloxy, n-octyloxy, etc. are mentioned.

[0022] It is A among monomers of the above-mentioned structural-formula (IV). [0023]



[Formula 15]

[0024] Come out and as a certain thing, for example beta-(meth)acryloyloxy ethoxysilane, gamma-(meta)

acryloyloxypropyl trimethoxysilane, gamma-(meta) acryloyloxypropyl triethoxysilane, gamma-(meta)

acryloyloxypropyl dimethoxysilane, gamma-(meta) acryloyloxypropyl methyldiethoxysilane, etc. can

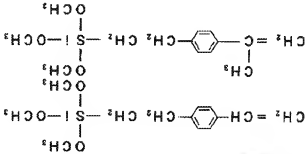
illustrate suitably.

[0025] It is A among the monomers of the above-mentioned structural-formula (IV). [0026]



[Formula 16]

[0027] coming out - as a certain thing - for example [0028]



[Formula 17]

[0029]**** is mentioned.

are mentioned, for example.

[0031] A which has one sort of functional groups chosen from a group of a carboxyl group, a sulfonic group,

and an amino group in this invention, and beta-ethylenic unsaturated monomer (c). As a monomer which raises

water solubility or water dispersibility of a copolymer, and has a carboxyl group, For example (meta), acrylic acid,

crotonic acid, itaconic acid, maleic acid, fumaric acid, 2-carboxy ethyl (meta) acrylate, 2-carboxy propyl (meta)

acrylate, an unsaturated monomer which has 5-carboxy pentyl (meta)- acrylate and a hydroxyl group, and

anhydrous 2 organic-functions carboxylic acid (for example, a maleic anhydride). An equimolar addition with

itaconic acid anhydride, a succinic anhydride, phthalic anhydride, etc., etc. are mentioned, and 2-(meta)

acryloxyethyl sulfonic acid etc. are mentioned as a monomer which has a sulfonic group, for example. As a

monomer which has an amino group, they are dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta)

acrylate, and t, for example. - Butylamino ethyl (meta) acrylate etc. are mentioned.

[0032] In this invention, as other copolymerizable alpha and beta-ethylenic unsaturated monomer (d), For

example, methyl acrylate (meta), ethyl acrylate (meta), acrylic acid (meta) n-propyl, (Meta) Acrylic acid isopropyl,

acrylic acid (meta) n-butyl, (Meta) Acrylic acid t-butyl, acrylic acid (meta) hexyl, (Meta) acrylic acid

2-ethylhexyl acrylate, acrylic acid (meta) n-octyl, (Meta) Decyl acrylate, acrylic acid (meta) lauryl, acrylic acid

(meta) stearyl, (Meta) Acrylic acid cyclohexyl, acrylic acid (meta) isobornyl, (Meta) Acrylic acid methoxy ethyl, acrylic acid (meta) ethoxyethyl, (Meta) Acrylic acid methoxy butyl, acrylic acid (meta) ethoxyethyl, (Meta) Acrylic acid 3-oxo-2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), (Meta) Ester of polyetherine polyol, such as acryloyl acid 3-acid 2-hydroxypropyl, acrylic acid 4-hydroxybutyl, a polyethylene glycol, and a polyethylene glycol, and acrylic acid (meta), which (meta) acrylic ester, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, t-butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, cyclohexyl vinyl ether, vinyl ether, such as phenyl vinyl ether, Propenyl ester, such as isopropenyl acetate, (Meta) Acrylonitrile, styrene, alpha - Methylstyrene, vinylene, alpha - KUROR styrene etc. are mentioned, and [for the purpose of one sort or two sorts or more], these can be chosen suitably and can be used.

[0033] A copolymerization ratio of the above-mentioned monomers preferably a monomer (a) three to 70% of the weight, 5 to 40 % of the weight, (b) 1 to 70 % of the weight, (c) three to 20% of the weight preferably one to 40% of the weight about 5 to 25% of the weight, and a monomer (d), since aqueous-izing of a copolymer or moisture powder-ization will become difficult if water repellence sufficient in less than 3 % of the weight is not acquired but a monomer (a) exceeds 70 % of the weight conversely, it is not desirable. Since it will arise and become easy to gel hydrolysis and a self-condensation reaction of alkoxysilyl groups to a polymerization process of a copolymer, or an aqueous-izing and moisture powder chemically-modified degree if a monomer (b) becomes poor [water solubility or water dispersibility of copolymer aqueous (moisture powder) liquid] in less than 1 % of the weight and exceeds 40 % of the weight conversely, it is not desirable. Since sufficient water repellence will not be acquired but a water resisting property will also fall remarkably further if aqueous-izing of a copolymer or moisture powder-ization becomes difficult and a monomer (c) exceeds 25 % of the weight conversely in less than 1 % of the weight, it is not desirable.

[0034] Copolymer solution or a water dispersion of this invention can be manufactured using a mixture of above-mentioned monomer (a) - (d) by methods, such as an emulsion polymerization method which use a neutralizer and uses aqueous-izing or a method of forming into moisture powder, and ** suggest-active agent after ** solution polymerization. From a water-repellent and waterproof point of a coat obtained [especially] by this invention, ** Add water and a neutralizer to it with a manufacturing method of aqueous-izing, copolymer solution which carries out moisture powder, or a water dispersion, after performing a method, i.e., an above-mentioned monomeric mixture, in an organic solvent, performing a radical polymerization under polymerization initiator existence and obtaining a copolymer (A) solution.

[0035] Copolymer solution or a water dispersion of this invention can be manufactured without using a surface-active agent for water repellence or a water resisting property for an adverse effect according to the manufacturing method of this invention.

[0036] In this invention method, as an organic solvent used at the time of a radical polymerization, it is desirable to be able to use an alcohol system, a cellulosic acetate system, a carbolic system, a cellulose acetate system, etc., and to contain alcohol of the carbon numbers 1-30% of the weight or more especially preferably 10% of the weight or more in an organic solvent. As a radical polymerization initiator, for example 2,2'-azobisisobutyronitrile, an initiator of peroxide systems, such as azo polymerization initiators, such as 2,2'-azobis (2,4-dimethylvaleronitrile), or lauryl peroxide, t-butyl par 2-ethyl hexanate, and benzoyl peroxide, can be used. This radical polymerization start agent concentration has 0.3 to 10 preferred weight section to monomer 100 weight section.

[0037] In this invention method, as a neutralizer used on the occasion of aqueous-izing or moisture powder, When a monomer (c) has a carboxyl group and a sulfonic group, For example, monomethylamine, dimethylamine, trimethylamine, monoethyl amine, Diethylamine, triethylamine, monoisopropylamine, diisopropylamine, Triisopropyl amine, monobutyl amine, dibutylamine, Monothanolamine, diethanolamine,

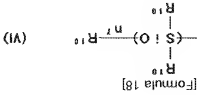
triethanolamine, aniline, such as dimethylamino ethanol and diethylamino ethanol. When ammonia, sodium hydroxide, a potassium hydride, etc. can be used and a monomer (c) has an amino group, organic acid, such as inorganic acid, such as chloric acid, sulfuric acid, and phosphoric acid, formic acid, acetic acid, propionic acid, trimethylacetic acid, acrylic acid (meta), lactic acid, can be used, for example.

[0038] A copolymer (A) obtained by the above-mentioned radical polymerization Aqueous-izing or when moisture powder is carried out. For example, after neutralizing by adding a neutralizer, agitating a copolymer (A) solution, it is also possible to carry out phase conversion of the copolymer (A) which added water or was neutralized by adding gradually undewater, but. In this case, since hydrolysis and a condensation reaction of alkoxy silyl groups is desirable to prevent it, it is desirable to perform neutralization and water addition as much as possible for a short time. Although time from neutralizer addition to phase conversion by water changes with a reaction vessel, churning conditions, and ambient temperature, specifically, generally, it is convenient to consider it as less than 10 hours preferably for less than 24 hours. It is the method of aqueous-izing or the most desirable method of carrying out moisture powder adding water in a copolymer (A) solution, and adding a neutralizer after that, without making the above-mentioned copolymer (A) solution thicken and gel. Since a neutralizer which acts also as a hydrolysis catalyst of alkoxy silyl groups, and promotes bridge construction is blended after moisture powder according to this method, and a silanol group may exist stably, thickening and gelling can be prevented.

[0039] In this invention method, after mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decantation is possible, water and a neutralizer are added, and into this mixture, it can water-grit, or can moisture-powder-ize, and can manufacture into it. [0040] As this resin (B), if it mixes with a copolymer (A) enough, there will be no restriction in particular. For example, a copolymer obtained by carrying out copolymerization of a monomer which gives water solubility/water dispersibility, and the other monomers, and a copolymer obtained by choosing it as said monomer (c) and a monomer (b), and (d) suitably from listings, and specifically carrying out copolymerization to them can be used. A copolymerization reaction can be performed like a copolymer (A).

[0041] As for a using rate of resin (B), when using the above-mentioned resin (B), it is preferably desirable in sum total resin solid content with a copolymer (A) to make it become 80 or less % of the weight 95 or less % of the weight. Since sufficient water repellence cannot be acquired if a using rate of this resin (B) exceeds 95 % of the weight, it is not desirable.

[0042] Furthermore, in this invention method, in order to raise water repellence in early stages of coat formation especially on the occasion of aqueous-izing of the above-mentioned copolymer (A), or formation of moisture powder, After adding a surface-active agent which has a water-repellent group in a mixed solution of a copolymer (A) solution or a copolymer (A), and resin (B), it can water-grit or water decantation. [0043] As this surface-active agent, what has a water-repellent group shown, for example by following structural-



[0045] (R¹⁰) shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n⁷ shows the integer of 5-200, respectively.)

$$[\text{Formula 19}] \quad \frac{-(C F_2)_n}{(W)}$$

[0047] Y shows a hydrogen atom or a fluorine atom among a formula, and n⁸ shows the integer of 1-30, respectively.) Specifically as a surface-active agent shown by following structural formula (VI), polyether modified silicone oil, alkyl modified silicone oil, etc. are mentioned, for example. Specifically as a surface-active agent shown by following structural formula (VII), perfluoroalkyl carboxylate, a perfluoro alkyl-sulfonic-acid salt, etc. are mentioned, for example. As for the addition of this surface-active agent, it is desirable that it is 5 or less % of the weight preferably 10 or less % of the weight to resin solid content. Since the water repellence and the water resisting property of a coat which will be obtained if this addition exceeds 10 % of the weight fall, it is not desirable.

[0048] On the other hand, by this invention, an emulsifier is used for this through a manufacturing method of the aforementioned **, i.e., water, distributed emulsification of the mixture of said monomer (a) - (d) is carried out, and an emulsion polymerization method performed by adding a water-soluble polymerization initiator and heating at 50-90 °C is also provided. If a redox initiator is used, it is also possible to carry out at a room temperature. As an emulsifier, for example anionic surface active agents, such as sulfate or higher alcohol, and an alkyl-sulfonic-acid salt, Nonionic surface active agents, such as various alkyl ether of a polyoxyethylene, alkyl ester, and alkyl allyl ether, a reactive surface active agent which has a polymerization nature unsaturation group, etc. are used. As a polymerization initiator, hydrogen peroxide, ammonium persulfate, cumene hydroperoxide, or a water-soluble redox initiator is used, for example.

[0049] Subsequently, in this invention, a distemper constituent which contains copolymer solution or a water dispersion manufactured as above-mentioned as a vehicle component is provided.

[0050] In a mixture of monomer (a) - (d) used for manufacture of the above-mentioned copolymer solution or a water dispersion, a monomer (e) which has a carbonyl group can be further contained five to 20% of the weight preferably one to 30% of the weight if needed from points, such as a water resisting property.

[0051] As a monomer (e) which has a carbonyl group, for example, an acrolein, diacetone acrylamide, diacetone methacrylamide, Vinyl alkyl ketone (for example, vinyl methyl ketone, vinyl ethyl ketone, vinyl butyl ketone) etc. which have acetooxyethylmethacrylate, formyl styrol, and 4-7 carbon atoms are mentioned.

Among these [especially], diacetone acrylamide and diacetone methacrylamide are preferred. [0052] The distemper constituent of this invention can contain a hydrazone derivative which has at least two -NH-NH₂ content groups in one molecule as a cross linking agent, when the above-mentioned carbonyl group is introduced into a copolymer. Hydrazone groups and a semicarbazide group are contained in a -NH-NH-NH₂ content

group here.

[0053] As this hydrazone derivative, for example Oxalic acid dihydrazone, malonic acid dihydrazone, Glutamic acid dihydrazone, amber acid dihydrazone, adipic acid dihydrazone, Saturated-fat fellows carboxylic acid dihydrazone which has 2-18 carbon atoms, such as sebacic acid dihydrazone, Maleic acid dihydrazone, Monocrotonic unsaturated-dicarboxylic-acid dihydrazone, such as fumamic acid dihydrazone and Itaconic acid dihydrazone;

Phthalic acid, Terephthalic acid or isophthalic acid dihydrazone, and dihydrazone of pyromellitic acid,

TORINHDORAJID or tetrahydrazone: Nit RIROTORI hydrazone, Tetrahydrazone citrate, 1,2,4-benzene

TORINHDORAJID, ethylene-diamine-tetraacetic acid tetrahydrazone, 1,4,5,8-naphtholic acid tetrahydrazone,

polyhydrazone which makes a low-grade polymer which has a carboxylic acid lower-alkyl-ester group come to react to hydrazone or a hydrazone hydrate (hydra JINHIDOLand) (refer to JP,5,2-22878,B); Carbonic dihydrazone,

Screw semicarbazide; A polyfunctional semicarbazide produced by making a hydrazone compound and a dihydrazone of the above-mentioned illustration react to a polyisocyanate compound derived from diisocyanate,

such as hexamethylene diisocyanate and isophorone diisocyanate, and it superfluously, a drainage system for polyfunctional semicarbazide produced by making dihydrazide of the above-mentioned illustration react to an isocyanate group in a reaction of the polyisocyanate compound and an active hydrogen compound and containing hydrophilic radicals, such as polyether polyol and polyethylene-glycols monoalkyl ether, superfluously. Or a mixture (refer to JP,8-151358 A and JP,8-245878 A) of this polyfunctional semicarbazide and a drainage system polyfunctional semicarbazide, etc. are mentioned.

[0054] This hydrazine derivative is blended so that 0.1-2 mol of -NH-NH_2 groups in a hydrazine derivative may be 0.05-1.5 mol preferably to 1 mol of a carbonyl group contained in said copolymer solution or a water dispersion. [0055] Further, if needed, additive agents for paints, such as pigments, a bulking agent, aggregates, a pigment agent, a wetting agent, a defoaming agent, a plasticizer, a film formation auxiliary agent, an organic solvent, an antiseptic, an antifungal agent, a pH adjuster, a rust-preventer, and a curing catalyst, can be chosen suitably, can be combined, and can be blended with a distemper constituent of this invention.

[0056]

[Example] Hereafter, an example is given and this invention is explained still in detail. A "weight section" and "% of the weight" are meant a "part" and "%", respectively.

[0057] Isopropyl alcohol 79 weight section was laught into the manufacture example 1 flask of a copolymer water dispersion, and temperature up was carried out, agitating to flowing-back temperature (about 84 °C).

Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature.

[0058]

Styrene Ten copies 58 copies of n-butyl methacrylate Acrylic acid Seven copies KBM-502 (notes 1) 15 copies

Silaplane FM-0711 (notes 2) Ten copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy]. It cools to a room temperature. The almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained. Then, the obtained copolymer solution was moved to the dilution tub, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously, carrying out temperature up to 50 °C and performing churning for 2 hours, keeping temperature at 50 °C, it cooled, and the colorless, almost transparent water dispersion of 10% of the nonvolatile matter was obtained.

[0059] KBM-502: Shin-Etsu Chemical Co., Ltd. make, an alkoxy-silyl-groups content monomer, Silaplane (notes 2) FM-0711: (Note 1) In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 1,000 example 2 Example 1. Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0060]

Styrene Ten copies 28 copies of n-butyl methacrylate Acrylic acid Seven copies Vinyltrimethoxysilane 15-copy Silaplane FM-0711 40 copies Azobisisobutyronitrile In one-copy example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0061]

Styrene Ten copies N-butyl methacrylate 58 copies Acrylic acid Seven copies KBM-503 (notes 3) 15 copies Silaplane FM-0725 (notes 4) Ten copies Azobisisobutyronitrile One-copy (notes 3) KBM-503: I Shin-Etsu Chemical Co., Ltd. make, an alkoxy-silyl-groups content monomer, Silaplane (notes 4) FM-0725: In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 10,000 example 4 Example 1. Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0062] Styrene Ten copies N-butyl methacrylate 62 copies Acrylic acid Seven copies KBM-502 Ten copies FAMAAC (notes 5) Ten copies Azobisisobutyronitrile One-copy (notes 5) FAMAAC : [Nippon Mektron, Ltd. make,] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as perfluorooctyl methacrylate and 60.7 % of the weight of fluorene concentration example 5 Example 1, and the almost water-white consistency copolymer solution of 56 % of the nonvolatile matter was obtained. Then, the series surface-active agent 0.4 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 °, and carrying out temperature up to 50 °, and the colorless, almost translucent water dispersion of 10 % of the nonvolatile matter was obtained.

[0063] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 6 Example 1, and the almost water-white consistency copolymer solution of 56 % of the nonvolatile matter was obtained. Then, the obtained resin solution was moved to the dilution tub, the "Fluorad FC-93" (Sunlitiono 3M make, fluorochelical surfactant) 0.15 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 ° after 820 copies of deionized water having added 8.8 copies of triethylamines continuously after that and carrying out temperature up to 50 °, and the colorless, almost translucent water dispersion of 10 % of the nonvolatile matter was obtained.

[0064] Isopropyl alcohol 79 weight section was taught into the example 7 flask, and temperature up was carried out, agitating to flowing-back temperature (about 84 °). Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature.

[0065] Styrene Ten copies 30 copies of n-butyl methacrylate Methyl methacrylate Ten copies Acrylic acid Five copies KBM-502 Ten copies Silplane F-M-0711 35 copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy], to a room temperature. It cooled and the almost water-white consistency copolymer solution (A) of 56 % of the nonvolatile matter was obtained. In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (B) of 56 % of the nonvolatile matter was obtained.

[0066] Styrene Five copies N-butyl methacrylate 26-copy methyl methacrylate 37 copies Acrylic acid 2-hydroxyethyl Seven copies Acrylic acid Ten copies KBM-502 15 copies Azobisisobutyronitrile 18 copies of copolymer solutions (A) obtained by the one-copy above like, And after teaching 162 copies of copolymer solutions (B) to a dilution tub, respectively and agitating them for 15 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 ° after 816 copies of deionized water having added 13.3 copies of triethylamines continuously and carrying out temperature up to 50 °, and the water dispersion of the opalescence of 10 % of a nonvolatile matter was obtained.

[0067] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 8 Example 1, and the almost water-white consistency copolymer solution (C) of 56 % of the nonvolatile matter was obtained.

[0068] In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (C), and the almost water-white consistency copolymer solution (D) of 56 % of the nonvolatile matter was obtained.

[0069]

N-butyl methacrylate 22 copies Methyl methacrylate 48 copies Acrylic acid 30 copies Azobisisobutyronitrile 108

copies of copolymer solutions (C) obtained by the one-copy above like, And after teaching 72 copies of copolymer solutions (D) to a dilution tub, respectively and agitating them for 15 minutes, it cooled, after performing churning for 2 hours, keeping temperature at 50 °, after 807.1 copies of deionized water having added 22.7 copies of triethylamines continuously and carrying out temperature up to 50 °, and the almost water-white water dispersion of 10% of the nonvolatile matter was obtained.

[0070]0.15 copy of dodecylbenzenesulfonic acid ammonium and 95 copies of deionized water were taught into the example 9 flask, and temperature up was carried out to 85 °. Then, after using the homomixer for 80 copies of water and distributing the following monomeric mixture, 1.0 copy of ammonium persulfate was added. The water dispersion was dropped into the flask over 5 hours, it was made to ripe for further 2 hours, and the emission of the opalescence of 39% of a nonvolatile matter was obtained. The obtained emission was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0071]

Acrylic acid n-butyl-, Copies [50.5] Acrylic Acid 2-Hydroxyethyl 3 Part Acrylic Acid 1 Part Silaplane FM-0711 10 Part KBM-503 10 Part Dodecylbenzenesulfonic Acid ammonium in 8.7-Copy Comparative Example 1 Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitable, generation of a coarse particle and sedimentation took place and the water dispersion of the good state was not obtained.

[0072]

Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Silaplane FM-0725 Ten copies Azobisisobutyronitrile in one-copy comparative example 2 Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitable, generation of a coarse particle and sedimentation took place and the water dispersion of the good state was not obtained.

[0073]

Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Ten copies of FAMA(C)s Azobisisobutyronitrile in one-copy comparative example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, the polymerization reaction was performed in the flask by the same operation as Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained.

[0074]

N-butyl methacrylate 22 copies Methyl methacrylate 38 copies Acrylic acid 30 copies Silaplane FM-0711 Ten copies Azobisisobutyronitrile The resin solution obtained continuously one copy is moved to a dilution tub, it cooled, after performing churning for 2 hours, keeping temperature at 50 ° after adding 787.8 copies of deionized water, and 42 copies of triethylamines and carrying out temperature up to 50 °, and the almost water-white solution of 10% of the nonvolatile matter was obtained.

[0075]In comparative example 4 Example 1, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion with almost translucent colorlessness of 10% of the nonvolatile matter was obtained.

[0076]

Styrene Ten copies N-butyl methacrylate 48 copies Methyl methacrylate 20 copies Acrylic acid Seven copies KBM-502 15 copies Azobisisobutyronitrile Ethylene-glycol-monobutyl-ether 70 weight section is taught into one-copy comparative example 5 flask. Temperature up was carried out agitating to 95 °. Subsequently, the following monomeric mixture was dropped for 4 hours, keeping temperature at 95 °.

[0077]

Methyl methacrylate 42.5 copies N-butyl methacrylate 12.5 copies Acrylic acid 15 Part Acrylic acid 4-hydroxybutyl 30 part Azobisisobutyronitrile After riping for 2 hours, keeping temperature at 95 ° after that [0.7 copy], it cools to a room temperature, After adding 21 copies of triethylamines as a neutralizer, it diluted with 45 copies of ethylene glycol monobutyl ether, and the almost water-white consistency resin solution of 43% of the nonvolatile matter was obtained. The obtained resin solution was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0078] 0.15 copy of dodecylbenzenesulfonic acid ammonium and 95 copies of deionized water were taught into the comparative example 6 flask, and temperature up was carried out to 85 °. Then, after using the homomixer for 80 copies of water and distributing the following monomeric mixture, 1.0 copy of ammonium persulfate was added. The water dispersion was dropped into the flask over 5 hours, it was made to ripe for further 2 hours, and the emulsion of the opalescence of 39% of a nonvolatile matter was obtained. The obtained emulsion was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0079] n-butyl methacrylate 25.5 copies Acrylic acid n-butyl, Copies [50.5] Acrylic Acid 2-Hydroxyethyl, 3 Part Acrylic Acid 1 Part Siliaplane FM-0711 20 Part Dodecylbenzenesulfonic Acid Ammonium Water Dispersion or Solution of Examples 1-9 and Comparative Examples 3-6 Obtained as 8.7-Copy System-Performance-Testing above, All show good water dispersibility.

These were painted by a 50-micrometer applicator to the glass plate, respectively, and after making it dry at 100 ° for 2 hours, the following system performance testing was presented.

A result is shown in Table 1.

[0080] (1) Paint film appearance : viewing estimated and O and a gloss ***** private seal **** thing were made into x for the good thing.

[0081] (2) Water repellence : the waterdrop of 0.03 cc of deionized water was formed on each coated plate, and the angle of contact of waterdrop was measured with the harmony chemicals company make KONTAKU tongue gun meter CCA type. It is shown that water repellence is so good that the numerical value of an angle of contact is large.

[0082] (3) Water resisting property : after ***** (ing) each coated plate to 20 ° waterworks for 6 hours, what O, a white bluish mark, and blistering are accepted to in what does not have abnormalities in the painted surface made into x.

[Table 1]

塗膜外観	実施例													比較例
	1	2	3	4	5	6	7	8	9	3	4	5	6	
耐水性 (°)	92	103	99	93	99	98	89	88	85	75	67	65	77	
耐水性	○	○	○	○	○	○	○	○	○	×	×	×	×	

表 1

[0084] In creation example 10 Example 1 of distemper, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0085] Styrene Ten copies 48 copies of n-butyl methacrylate Diacetone acrylamide Ten copies Acrylic acid Seven copies KBM-502 15 copies Siliaplane FM-0711 Ten copies Azobisisobutyronitrile To the water dispersion obtained one

copy. 5.2 copies of adipic acid dihydrazide was added, it mixed, and the clear coating material was obtained. After painting this by a 50-micrometer applicator to the glass plate and making it dry at 100 ° for 2 hours, when the same system performance testing as the above was presented, paint film appearance and the water resisting property of all were O, and the water contact angle was 93 degrees.

[0086]

[Function and Effect(s) of the invention] In the copolymer solution or the water dispersion of this invention, The alkoxy silyl groups introduced into the copolymer by using a monomer (b) as a copolymerization ingredient hydrolyzes under existence of water, and turns into a silanol group, it can conquer, in order that this silanol group may raise water solubility or water dispersibility remarkably, and it can become possible to lessen the amount of copolymerization of the monomer (c) which has a functional group which moreover gives water solubility/water dispersibility, and water repellence can be raised. In the drying process of the coat by this copolymer solution or a water dispersion, in order to form the firm structure of cross linkage by the self-condensation reaction of silanol groups, the coat which shows a good water resisting property is obtained.

[0087] Therefore, the diisocyanate constituent using the copolymer solution or the water dispersion of this invention as a vehicle component can form the coat excellent in water repellence and a water resisting property.

[Translation done.]

[illegible]

Abstract of JP11124419

[View INPADOC patent family](#)

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Classification

Applicant:

INVENTOR

Publication date: 1999-05-11

WATER-REPELLING PROPERTY, ITS PRODUCTION AND AQUEOUS COATING COMPOSITION CONTAINING THE SAME

特開平11-124419

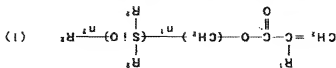
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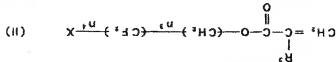
(54) 【発明の名称】 親水性を有する共重合体水溶液もしくは水分散液、及びその製造方法、及びこれを含む水性塗料組成物

(57) 【要約】
 【課題】 親水性及び耐水性に優れた塗膜を形成し得る塗料用樹脂として有用な共重合体水溶液もしくは水分散液及びその製造方法、及びこれを含む水性塗料組成物を提供すること。
 【解決手段】 (a) 2種の親水性を付与する単量体から選ばれる少なくとも1種の単量体を3〜70重量%、(b) アルコキシシリル基を有する単量体を1〜40重量%、(c) カルボキシル基、アルボノ酸基及びアミノ基の群から選ばれる1種の官能基を有するα、β-エチレン性不飽和単量体を1〜25重量%、および (d) その他の共重合可能なα、β-エチレン性不飽和単量体を0〜95重量%含有する単量体混合物を共重合する。



00の数を失くす。

【0008】



【化10】

【0007】(式中、R¹は水素原子又はメチル基、R²は同一又は異なるフエニル基又は炭素数1〜6のアルキル基、n¹は1〜10の数、n²は5〜2

【0009】(式中、R²は水素原子又はメチル基、Xは水素原子又はフッ素原子、n¹は1〜8の数、n²は1〜30の数、失くす。

(b)アリルキシリル基を有する単体を1〜40重量%、(c)カルボキシル基、アミノ基及びフェニル基の官能基を有するα、β-エチレン性不飽和単体を1〜25重量%、および(d)その他の共重合可能なα、β-エチレン性不飽和単体を0〜95重量%含有する単体混合物を共重合すること

を特徴とする親水性を有する共重合体水溶液もしくは分散液、及びその製造方法、及び該共重合体水溶液もしくは分散液を有する水性塗料組成物を提供するものである。

【0010】発明において上記の構造式(1)及び(11)で示される単体から選ばれる少なくとも1種の単体(a)は、共重合体に親水性を付与するものである。上記構造式(1)で示されるポリロキソレンを有する単体(a-1)及び上記構造式(11)で示されるポリロキソレンを有する単体(a-2)のいずれか1方又は両方を使用できる。

【0011】上記構造式(1)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。n²が5未満では十分な親水性が得られず、逆に200を越える場合は共重合体の親水性が不足し、親水性もしくは水分散性不良となるので適当な範囲である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0012】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0013】本発明において上記の構造式(1)及び(11)で示される単体(a)は、共重合体に親水性を付与するものである。上記構造式(1)で示されるポリロキソレンを有する単体(a-1)及び上記構造式(11)で示されるポリロキソレンを有する単体(a-2)のいずれか1方又は両方を使用できる。

【0014】上記構造式(1)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0015】(式中、R¹は炭素数1〜10のアルキル基を有する単体、R²は同一又は異なるフエニル基、炭素数1〜6のアルキル基又は炭素数1〜10のアルキル基を有する単体、n¹は1〜4の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0016】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0017】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0018】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0019】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0020】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0021】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0022】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0023】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

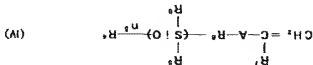
【0024】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0025】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0026】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

【0027】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。

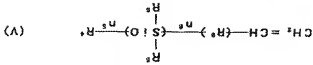
【0028】上記構造式(11)で示される単体(a-1)において、R¹は水素原子またはメチル基である。R²はフェニル基または炭素数1〜6のアルキル基であるが、必ずしも互いに関しものである必要はない、n¹は1〜10の数、n²は5〜200、好ましくは15〜150の数である。該単体(a-1)の具体例として、市販品では、「サトラブレンF-M-0711」、「サトラブレンF-M-0721」、「サトラブレンF-M-0725」(いずれもサトラブレン)等が挙げられる。




【0019】を示す。R¹は水素原子又はメチル基を、R²は炭素数1～6の2価の脂肪族飽和炭化水素基を夫

々示す。R⁴、R⁵、R⁶及びn⁵は、夫々前記と同じ意味を有する。）

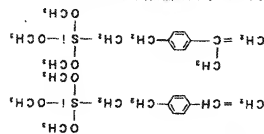
【4】



1976
1977



[0028]



【0029】なにか知られろ。

冬令キエ工日ナレニ、今冬令キエノ工日ニ對シテ、
22、'計'ツツモ事(ハ)ノ可解工【0800】

【0031】本発明にお

炭素及びアミノ基の群から選ばれた1種の官能基を有す

の溶解性として、水分散性を向上させるものであり、カ

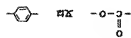
「 α 」は、 α 系を有する単量体として、例えば (メタ)

2-カルボキシルエチル(メタ)アクリレート

1. 2-カルボキシルプロピル (×2) アクリレート、
5-カルボキシルペンチル (×2) アクリレート、水酸

性を有する不飽和単量体と無水2官能カルボン酸（例え

【0017】(系中、A注、
【0018】
【化13】



【0021】(式中、 R^3 は炭素数1～6の脂肪族飽和炭化水素基を、 n^5 は0又は1を示す、 R^4 、 R^5 及び n^5 は、夫々前記と同じ意味を有する。)

上記構造式 (IV) 及び (V) において、R³ 及び R⁹ に

基として、直鎖又は分枝状のアルキル基、例えば

[illegible]

ハ、ベンタメチレン、ヘキサメチレン基などを挙げられ

としては、直線又は分枝状のアルキル基、例えばメチ

[illegible]

ノベチル、ホオベチル、ロヘキシル、イノヘキシ

1. $I = -8$ ナルニナルニ付テハ、 R^0 示シ
 2. 炭素数 1~10 ナルニ付テハ、 R^0 及び R

で示される炭素数1~6のアルキル基として例示した

[illegible]

られる。R⁵及びR⁶で示される炭素数1~10のアルコキシル基としては、直鎖又は分枝状のアルコキシル

基、例えはメトキシ、エトキシ、n-プロポキシ、イソ

11654-11655, 11656-11657, 11658-11659, 11660-11661, 11662-11663, 11664-11665, 11666-11667, 11668-11669, 11670-11671, 11672-11673, 11674-11675, 11676-11677, 11678-11679, 11680-11681, 11682-11683, 11684-11685, 11686-11687, 11688-11689, 11690-11691, 11692-11693, 11694-11695, 11696-11697, 11698-11699, 11700-11701, 11702-11703, 11704-11705, 11706-11707, 11708-11709, 11710-11711, 11712-11713, 11714-11715, 11716-11717, 11718-11719, 11720-11721, 11722-11723, 11724-11725, 11726-11727, 11728-11729, 11730-11731, 11732-11733, 11734-11735, 11736-11737, 11738-11739, 11740-11741, 11742-11743, 11744-11745, 11746-11747, 11748-11749, 11750-11751, 11752-11753, 11754-11755, 11756-11757, 11758-11759, 11760-11761, 11762-11763, 11764-11765, 11766-11767, 11768-11769, 11770-11771, 11772-11773, 11774-11775, 11776-11777, 11778-11779, 11780-11781, 11782-11783, 11784-11785, 11786-11787, 11788-11789, 11790-11791, 11792-11793, 11794-11795, 11796-11797, 11798-11799, 11800-11801, 11802-11803, 11804-11805, 11806-11807, 11808-11809, 11810-11811, 11812-11813, 11814-11815, 11816-11817, 11818-11819, 11820-11821, 11822-11823, 11824-11825, 11826-11827, 11828-11829, 11830-11831, 11832-11833, 11834-11835, 11836-11837, 11838-11839, 11840-11841, 11842-11843, 11844-11845, 11846-11847, 11848-11849, 11850-11851, 11852-11853, 11854-11855, 11856-11857, 11858-11859, 11860-11861, 11862-11863, 11864-11865, 11866-11867, 11868-11869, 11870-11871, 11872-11873, 11874-11875, 11876-11877, 11878-11879, 11880-11881, 11882-11883, 11884-11885, 11886-11887, 11888-11889, 11890-11891, 11892-11893, 11894-11895, 11896-11897, 11898-11899, 11900-11901, 11902-11903, 11904-11905, 11906-11907, 11908-11909, 11910-11911, 11912-11913, 11914-11915, 11916-11917, 11918-11919, 11920-11921, 11922-11923, 11924-11925, 11926-11927, 11928-11929, 11930-11931, 11932-11933, 11934-11935, 11936-11937, 11938-11939, 11940-11941, 11942-11943, 11944-11945, 11946-11947, 11948-11949, 11950-11951, 11952-11953, 11954-11955, 11956-11957, 11958-11959, 11960-11961, 11962-11963, 11964-11965, 11966-11967, 11968-11969, 11970-11971, 11972-11973, 11974-11975, 11976-11977, 11978-11979, 11980-11981, 11982-11983, 11984-11985, 11986-11987, 11988-11989, 11990-11991, 11992-11993, 11994-11995, 11996-11997, 11998-11999, 12000-12001, 12002-12003, 12004-12005, 12006-12007, 12008-12009, 12010-12011, 12012-12013, 12014-12015, 12016-12017, 12018-12019, 12020-12021, 12022-12023, 12024-12025, 12026-12027, 12028-12029, 12030-12031, 12032-12033, 12034-12035, 12036-12037, 12038-12039, 12040-12041, 12042-12043, 12044-12045, 12046-12047, 12048-12049, 12050-12051, 12052-12053, 12054-12055, 12056-12057, 12058-12059, 12060-12061, 12062-12063, 12064-12065, 12066-12067, 12068-12069, 12070-12071, 12072-12073, 12074-12075, 12076-12077, 12078-12079, 12080-12081, 12082-12083, 12084-12085, 12086-12087, 12088-12089, 12090-12091, 12092-12093, 12094-12095, 12096-12097, 12098-12099, 12100-12101, 12102-12103, 12104-12105, 12106-12107, 12108-12109, 12110-12111, 12112-12113, 12114-12115, 12116-12117, 12118-12119, 12120-12121, 12122-12123, 12124-12125, 12126-12127, 12128-12129, 12130-12131, 12132-12133, 12134-12135, 12136-12137, 12138-12139, 12140-12141, 12142-12143, 12144-12145, 12146-12147, 12148-12149, 12150-12151, 12152-12153, 12154-12155, 12156-12157, 12158-12159, 12160-12161, 12162-12163, 12164-12165, 12166-12167, 12168-12169, 12170-12171, 12172-12173, 12174-12175, 12176-12177, 12178-12179, 12180-12181, 12182-12183, 12184-12185, 12186-12187, 12188-12189, 12190-12191, 12192-12193, 12194-12195, 12196-12197, 12198-12199, 12200-12201, 12202-12203, 12204-12205, 12206-12207, 12208-12209, 12210-12211, 12212-12213, 12214-12215, 12216-12217, 12218-12219, 12220-12221, 12222-12223, 12224-12225, 12226-12227, 12228-12229, 12230-12231, 12232-12233, 12234-12235, 12236-12237, 12238-12239, 12240-12241, 12242-12243, 12244-12245, 12246-12247, 12248-12249, 12250-12251, 12252-12253, 12254-12255, 12256-12257, 12258-12259, 12260-12261, 12262-12263, 12264-12265, 12266-12267, 12268-12269, 12270-12271, 12272-12273, 12274-12275, 12276-12277, 12278-12279, 12280-12281, 12282-12283,

オキシ、イソヘキシルオキシ、ノオクチルオキシなど

【0022】上記構造式(IV)の単量体のうちAが

【0023】
【415】

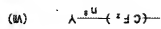
0

-C-0-

$$G_2(GX) = L \cdot G_2(GX) = L \cdot G_2(GX) = L \cdot G_2(GX)$$

[illegible][illegible]

【0038】上記ゾリル重合によって得られた共重合体(A)を水酸化もしくは水分散する場合、例えば共重合体(A)溶液を精製しながら中和剤を添加して中和した後、水を添加するが、中和した共重合体(A)を水中に懸けながら相転換することも可能である。この場合アルコキシシリル基の加水分解及び凝合が、反応が急速に行し、増粘、ゲル化すおそれがあるため、それを防止するために中和及び水添加をできるだけ短時間で行うことが望ましい。具体的には、中和剤添加から水による相転換までの時間は、反応容器、攪拌棒、管間温度によって異なるが、一般には24時間以内、好ましくは10時間以内とするのが好都合である。上記共重合体(A)溶液を、増粘もしくはゲル化し、水溶液化もしくは水分散させるも好ましい方法は、共重合体(A)溶液を添加し、その後に中和剤を添加する方法である。この方法によればアルコキシシリル基の加水分解凝結としても作用し架橋を促進する中和剤が水分散液中から凝出、ゲル化を防止できる。【0039】また本発明方法においては、(A)溶液に、親水性基を含まない水酸化もしくは水酸化可能な樹脂(B)溶液を混合してから、該混合液に水および中和剤を添加し水酸化もしくは水分散化して得ることができる。【0040】樹脂(B)としては、共重合体(A)と十分混合するものであれば特に制限はなく、例えば水溶性分散性を持つ単体及びその単体の共重合体を共重合体(C)及び単体(B)、(D)に列記の中から選択することにより得られる共重合体と併用することができる。【0041】上記樹脂(B)を用いる場合、樹脂(B)同様にして行なうことができる。【0042】さらに本発明方法において、上記共重合体(A)の水酸化もしくは水分散化に際して特に酸鹼形成初期の親水性を向上させる目的で、共重合体(A)溶液もしくは共重合体(A)及び樹脂(B)の混合溶液に親水性基を有する界面活性剤を添加してから水酸化もしくは水分散化することとができる。【0043】該界面活性剤としては、例えば下記構造式(Ⅷ)または(Ⅸ)と示される親水性基を有するものを使用してできる。【0044】【化18】



【0045】(式中、R¹⁰は7ニル基又は炭素数1〜6の7ニル基を、n⁷は5〜200の整数を夫々示す。)



【0047】(式中、Yは水素原子又は7ニル基原子を、n⁷は1〜300の整数を夫々示す。)

【0048】一方本発明では、前記の製造方法、即ち水を媒体として、これに乳化剤を用いて前記単量体(A)〜(D)の混合物を分散乳化させ、水溶性の重合開始剤を加えて50〜90℃で加熱することによって行われ乳化重合法も提供することである。レックス剤を用いると速度で行なうことも可能である。乳化剤としては、例えば高級アルコールの硫酸塩、アルキルアルコールの各種アルキルエーテル、アルキルエステル、アルキルアミンなどの非イオン界面活性剤、及び酸性非飽和基を有する反応性界面活性剤などを使用される。重合開始剤としては、例えば過酸化水素、過硫酸アモニウム、クメンヒドロパーオキシド、あるいは水溶性レックス剤などが用いられる。【0049】改い本発明では、上記の通り製造される共重合体水溶液もしくは水分散液をレックス成分として含む水性塗料組成物を提供するものである。【0050】上記共重合体水溶液もしくは水分散液の製造に用いられる単体(A)〜(D)の混合割合は、さらに親水性を有するからカルビニル基を有する単体から必要に応じて1〜30重量%、好ましくは5〜20重量%を有することができ、【0051】カルビニル基を有する単体(e)として、例えばクロトン、メタクリルモノマー、アセトキシエチルメタクリレート、ホルミルアクリレート、4〜7個

$$16 \div 4 = 4$$

【0060】
車重減低物を用いた例として同様に、
100%、不揮発分10%のうす乳白色の水分散液を得た。

【0061】

い、不揮発分10%のうすい乳白色の水分散液を得た。

40部
1部

(注4)

実施例4において、減下する車体混合物として下記の車体混合物を用い、ひけは実施例1と同様にして行

い、不揮発分10%のうすい乳白色の水分散液を得た。

10部
58部
7部
15部
10部
1部

【0062】

10部

62部

7部

10部

10部

1部

プラスチック中で重合反応を行い、不揮発分56%のほぼ無色

透明の粘稠な共重合体溶液を得た。続いて得られた樹脂

溶液を希釈槽に移し、「フロラ-FC-93」(住友

スリエム社製、アーク界面活性剤)0.15部を添

加して10分間撹拌した。その後脱イソノ水820部、

続いてトリエチルアミン9.8部を加えて50℃に昇温

したのち温度を50℃に保ちながら2時間撹拌を行っ

から冷却し、不揮発分10%のほぼ無色の半透明な水分

散液を得た。

【0064】実施例7

プラスチック中にイソノアルコール7重量部を仕込

み、温度(約84℃)まで撹拌を行いつながら昇温し

た。次いで温度を還元温度に保ちながら下記車体混合

物を4時間減下した。

【0065】

10部

30部

10部

5部

10部

33部

1部

液(A)と同様にして重合反応を行い、不揮発分56%

のほぼ無色透明の粘稠な共重合体溶液(B)を得た。

【0066】

5部

26部

サトアブレン-PM-0711
アビスアノアノクロトリル

実施例3において、減下する車体混合物として下記の車体混合物を用い、ひけは実施例1と同様にして行

アビスアノアノクロトリル

アビスアノアノクロトリル

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車体混合物を用いた以外は実施例1と同様の操作で、ラスコ中で重合反応を行い、不揮発分5.6%のほぼ無色の樹脂を得た。

【0074】

実施例1において、適する車体混合物として下記の車体混合物を用いた以外は実施例1と同様に行い、不揮発分1.0%のほぼ無色の半透明な水分散液を得た。

【0076】

10部
48部
20部
7部
15部
1部

を4時間滴下した。

【0077】

4.2部
1.5部
12.5部
30部
0.7部

0.1部と脱酸素水9.5部を仕込み、8.5℃に昇温した。続いて下記の車体混合物を水80部にホモミキサーを用いて分散してから過硫酸アモニウム1.0部を追加した。その水分分散液を5時間かけてラスコ中に滴下し、さらに2時間反応させて不揮発分3.9%の乳白色のエマルジョンを得た。得られたエマルジョンは脱酸素水で不揮発分1.0%に希釈して性能試験に用いた。

【0079】

2.5部
50.5部
3部
1部
20部
8.7部

性能試験
上記の通り得られた実施例1～9および比較例3～6の水分散液も、これはガラス瓶に50mLずつ入れ、100℃で2時間乾燥させた後、下記の方法で試験に供した。結果を表1に示す。

【0080】(表1) 塗膜外觀：目視で詳細し、良好なものも○、ツヤ付が認められるものを×とした。

【0081】(表2) 排水性：各塗膜上に0.03

【0083】

【表1】

表1

比較例		実施例									
耐水性	○	○	○	○	○	○	○	○	○	○	○
耐水性(%)	92	103	95	93	99	98	89	85	75	87	85
耐水性	○	○	○	○	○	○	○	○	○	○	×
耐水性	1	2	3	4	5	6	7	8	9	3	4
比較例	5	6	7	8	9	10	11	12	13	14	15

い、不揮発分10%のほぼ無色の半透明な水分散液を得

た。

【0085】

実施例1において、滴下する単量体混合物として下記の単量体混合物を用いた以外は実施例1と同様にして行

スチレン

メタクリル酸-n-ブチル

メタセトブチルアクリレート

アクリル酸

KBM-502

γ-ブチロラクトン

γ-ブチロラクトン

得られた水分散液に、アクリル酸とKPSを、2部

を加えて混合してポリマー原料を得た。これをガラス板

に50μmアクリルシートで被覆し、100℃で2時間

乾燥させた後、上記と同様の性能試験に供したところ、

試験片は9

3であった。

【0086】

【作用及び発明の効果】本発明の共重合体水溶液もしくは

水分散液では、単量体(a)により導入された親水性

基による水溶性、水分散の難しさを、単量体(b)を共

重合成分とすることで共重合体中に導入されたアルコキ

シシリ基が水の存在下で加水分解してシラノール基と

フロントページの続き

(5) InL Cl²

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A

なり、このシラノール基が水溶性もしくは水分散性を帯
び、向上させるために足量で、しかも水溶性/水分散
性を付与する官能基を有する単量体(c)の共重合量を
少なくすることが可能となり親水性を向上させることが
できる。また該共重合体水溶液もしくは水分散液による
塗膜の乾燥過程においては、シラノール基同士の間
が反応により強固な架橋構造を形成するため、良好な耐
水性を示す塗膜が得られる。
【0087】従って本発明の共重合体水溶液もしくは水
分散液を、ビニル成分として用いた水性塗料組成物は、
親水性及び耐水性に優れた塗膜を形成することができ
る。